PATENT
1517-0138P

IN THE U.S. PATENT AND TRADEMARK OFFICE

In re Patent Application of:
Yasuhiro AYUKAWA et al.

Application No.: 10/099,953 Confirmation No.: 6331

Filed: March 19, 2002 Art Unit: 1743

For: PREPARATION OF AN OIL SAMPLE FOR X-RAY FLUORESCENCE ANALYSIS Examiner: Y. G. Gakh

DECLARATION UNDER 37 C.F.R. §1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Hisayuki Kohno, do declare and say as follows:

1. I am familiar with the contents of U.S. Patent Application Serial No. 10/099,953, filed March 19, 2002, its prosecution before the U.S. Patent and Trademark Office, and the references cited therein. I am Directer of Rigaku Industrial Corporation holding the position of Vice President, Tech Marketing and Application- XRF.

2. To show the superiority of the present invention, I am submitting the following observations:

(i) A skilled inventor can practice the present invention according to the disclosure without undue experimentation. The corresponding Japanese application has already been granted (Japanese Patent No. 3695651) without enablement being brought into question. Although the Examiner has raised questions about the English translation, there are no substantive differences between the United States Application and the corresponding Japanese application in disclosing the invention.

(ii) As evidence that the invention can be practiced by one of ordinary skill without undue experimentation, please find attached the *Handbook Of Petroleum*, pages 145-147 and 151-152, with the corresponding English translation[1]. The description in the attached Handbook Of Petroleum was made by the present inventors when they were employees of Rigaku.

In this technology, sulfur compounds contained in petroleum as impurities (page 145 of the *Handbook Of Petroleum*) are decomposed by x-ray radiation to be captured by sulfur-capturing liquid of the present invention (pages 146 and 147 of the *Handbook Of Petroleum*). This technology described in the *Handbook Of Petroleum* is substantially the same as that described in the specification.

As disclosed in the specification of the present invention, sulfur components contained in petroleum are changed to silver sulfide compounds and analyzed using fluorescent x-rays. The decomposition of sulfur compounds is performed using x-ray radiation. Fluorescent x-rays do not play a role in the decomposition reaction. Therefore, the main chemical reaction in the process of the present invention is that sulfur components decomposed by x-ray radiation react with silver nitrate contained in the sulfur capturing liquid to produce the precipitates of silver sulfide compounds.

When the capturing liquid of the present invention is prepared, the precipitate generated from impurities contained in raw reagents and the small amount of accidentally generated silver acetate precipitates are removed from the prepared solution. Since such precipitates are present

[1] Note that the description: "This technique is patented under a Rigaku patent" on page 146 of the Handbook really means that a patent application has already been filed. Also, the caption "Cat" on page 146 stands for "catalyst."

in small amounts, silver nitrate remains in large part in the solution. As a result, the silver nitrate can capture the sulfur components contained in petroleum.

Also, the embodiments of the upward or downward irradiation are shown in Figure 3 of the present application. Either the upward or downward irradiation configuration may be used in the present invention. A comparison of the upward and downward irradiation is described at page 151 of the *Handbook Of Petroleum*. The results show that either upward or downward irradiation can be used (Note that the term "downward irradiation" is expressed as "top irradiation" and the term "upward irradiation" is expressed by "bottom irradiation" in the English translation of the *Handbook Of Petroleum*. However, the meanings are the same.).

Further, the method for capturing sulfur of the present invention is quantitative, as is shown in Figure 6 of the application and in Table 2 of the specification.

As a result, the specification is clear and the invention is sufficiently enabled so it may be practiced without undue experimentation.

3. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

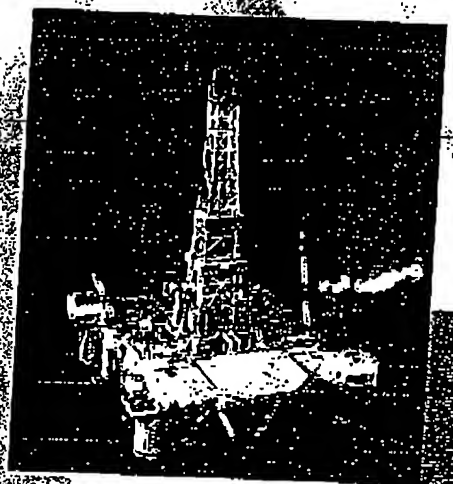
June 30, 2006
Date

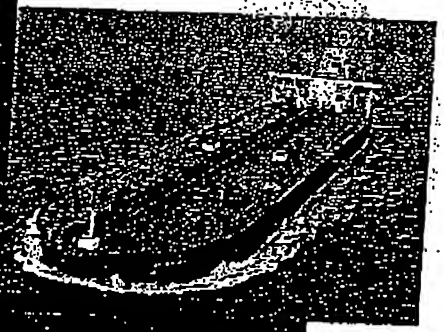
By Hisayuki Kohmi

Attachment: *Handbook Of Petroleum*, pages 145-147 and 151-152, with the corresponding English translation.

石油ハンドブック

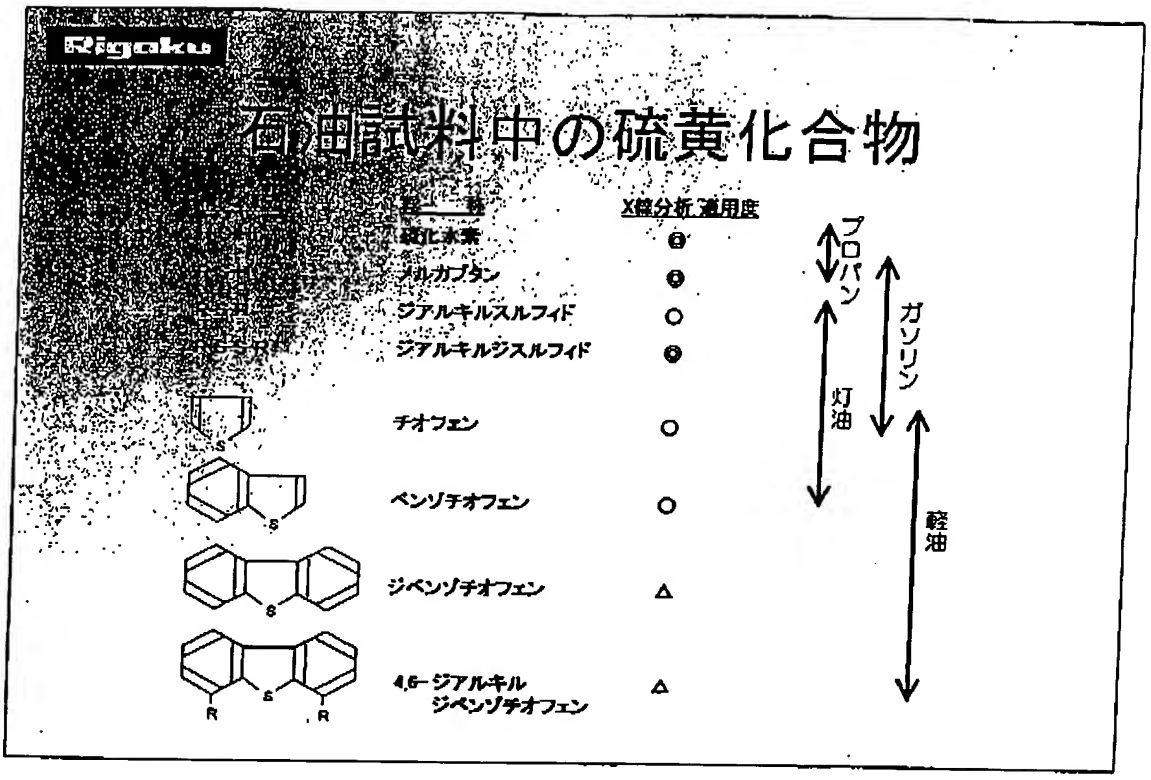
（社員用）





写真提供 石油連盟

理学電機工業株式会社 リガク

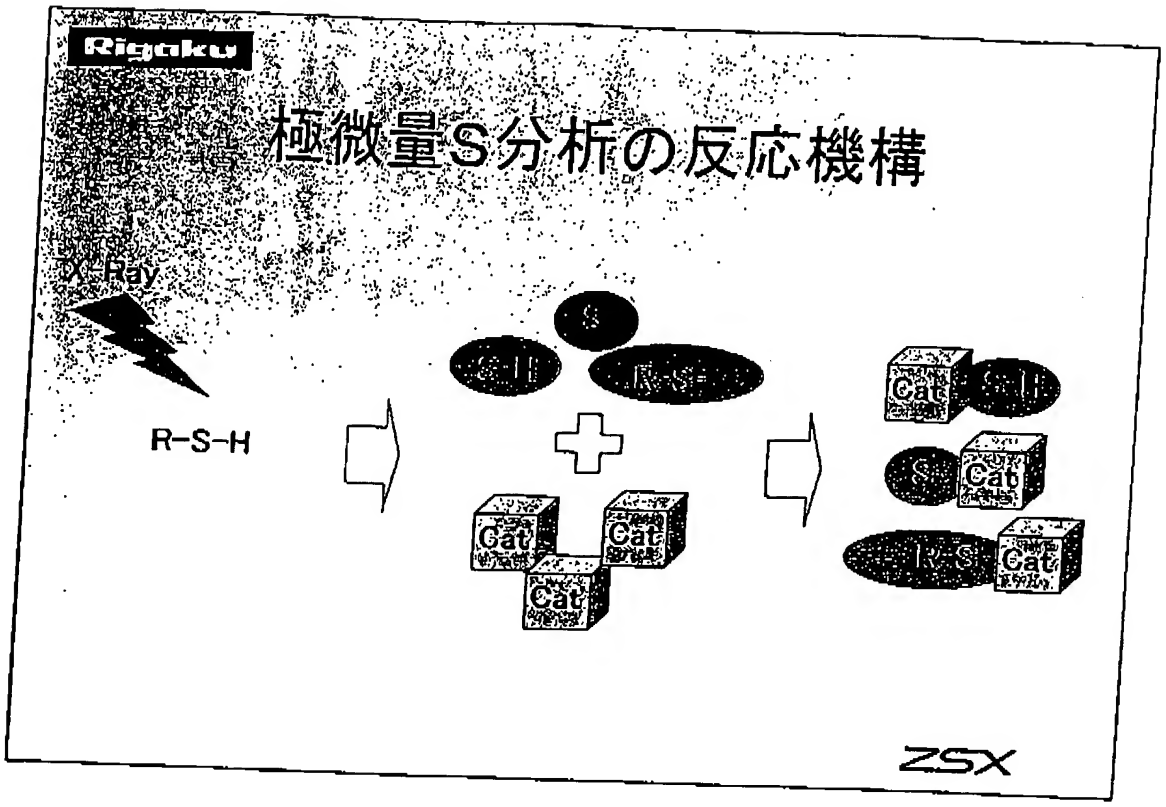


石油製品／半製品には、いろいろな形態の硫黄化合物が存在します。

例えば、家庭用の燃料として使用されます液化石油ガス(LPG)の中には、硫化水素やメルカプタンが存在します。

また、ガソリンには、メルカプタンやジアルキルスルフィドが多く存在しますが、最近のガソリンには改質ナフサが使用され、チオフェンが存在するものも数多くあります。

軽油の中には、チオフェンからジベンゾチオフェンまでが含まれ、その中でも、4,6-ジベンゾチオフェンは脱硫が難しい化合物と言われています。

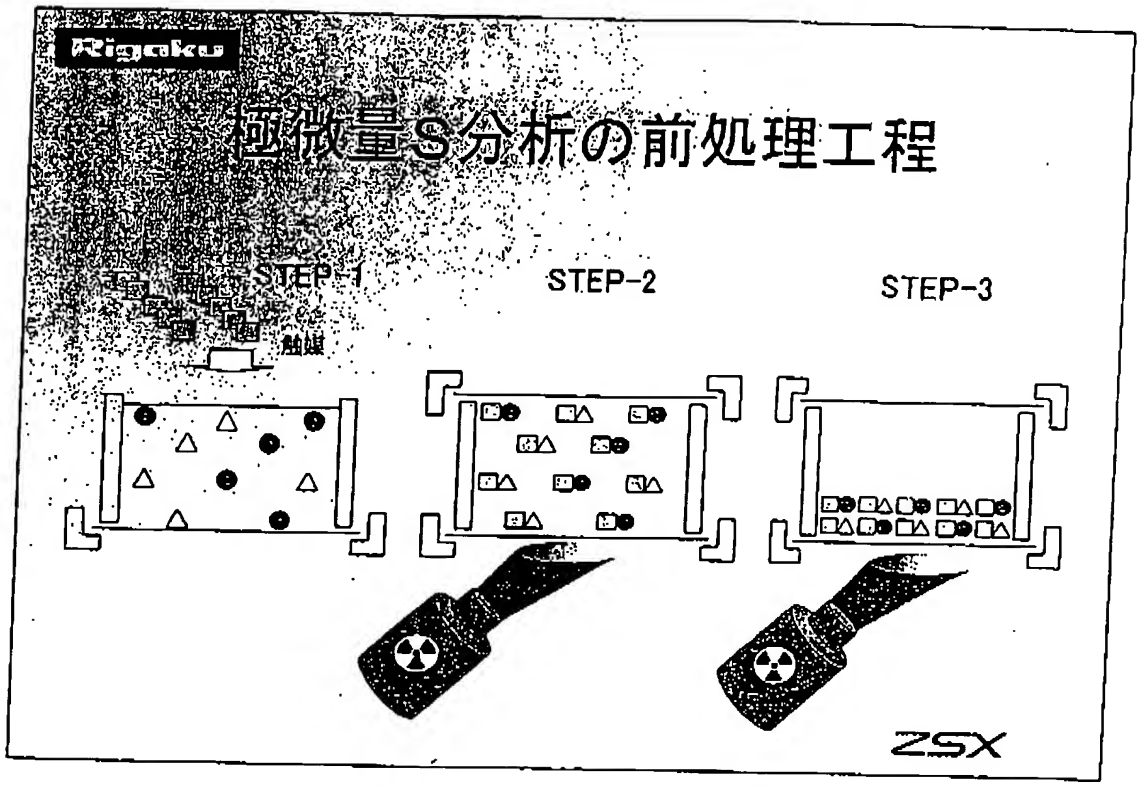


極微量(ppb)のＳ分析を行う場合、理学では前処理を行いＳ分を捕集して分析する手法を用いています。

この手法は、理学の特許です。

全容を紹介しますと、試料中に含まれる硫黄化合物を強力なＸ線で分解し活性化させます。そこに、触媒を用いて活性化されたＳ分とを反応させ、反応させたＳ分を触媒と共に捕集します。

この捕集したＳ分を測定する分析手法を用いることで、数ppbレベルの分析が可能となりました。



極微量のＳ分析手法をもう少し詳細に説明します。

STEP-1

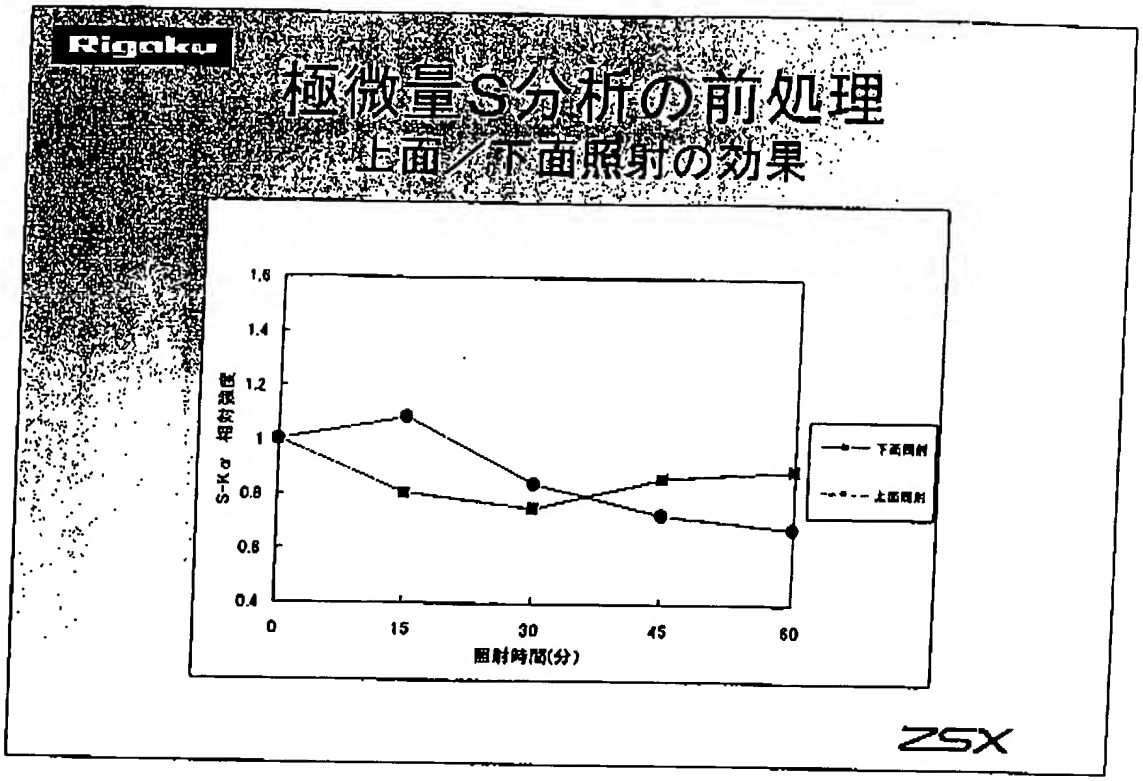
測定試料の中に、Ｓ分を回収させる触媒（理学製）を添加します。

STEP-2

この状態で、強力なＸ線を照射します。すると、試料中に含まれるＳ分は、Ｘ線によって分解され活性化されます。同時に、近隣に存在する触媒と反応し新しい化合物を形成します。

STEP-3

新しい硫黄化合物は、試料容器の底部に捕集され、その状態でＸ線分析を行います。試料中の硫黄化合物は、濃縮された状態になりますので、極微量領域のＳ分析が可能となります。

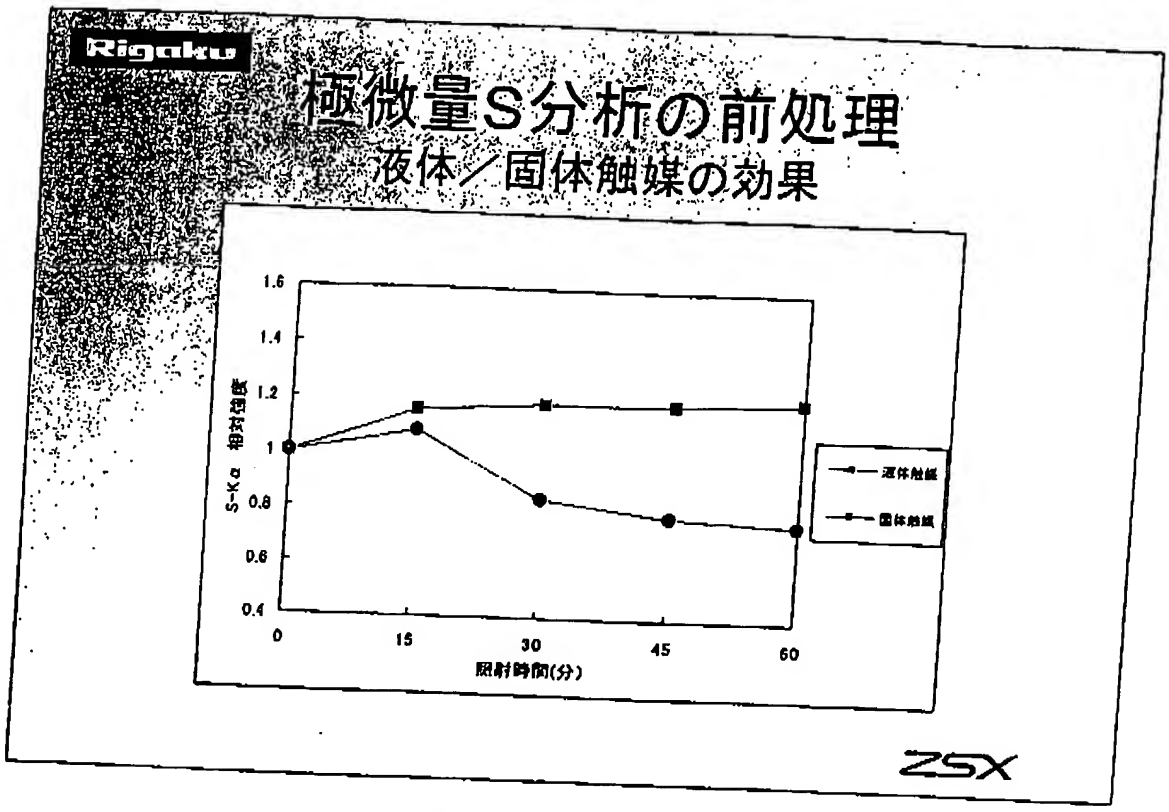


試料中の硫黄化合物と触媒とを反応させる時にX線を照射します。X線の照射方法も、上面から照射する場合と下面から照射する場合とがあります。

ここでは、それらの効果をグラフにしたものです。相対強度が低いものほど、触媒との反応が顕著であり効果的であることを意味します。

下面から照射しますと、照射直後から効果は現れますが、30分以上照射しますと効果は少なくなります。しかし、上面から照射した場合には、長時間（60分）照射しても、その効果は時間の経過と共に顕著に現れます。

従って、上面照射が最適ですが、下面照射の場合でも、30分の照射時間に限定すれば問題無く測定できます。



硫黄化合物を捕集する触媒の効果を示したグラフです。

硫黄化合物と触媒とを反応させ試料中に残った硫黄分を調査した結果です。検出強度が少ない方が効果が顕著であることを意味します。

ここでは、固体触媒と液体触媒との捕集効果を観察した事例です。

固体触媒を用いた場合には、この効果は殆ど観られません。しかし、液体触媒を使用しますと効果は顕著に現われます。

従って、反応効率を良くする場合には、液体触媒を選択する方が効果的だと言えます。

石油ハンドブック(社員用) [非売品]

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Handbook of Petroleum

(for Employees Only)

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Photos furnished by
Petroleum Association of Japan

Rigaku Industrial Corporation

Rigaku Corporation

Rigaku

Sulfuric Compounds in Petrochemical Samples

Structure	Generic Terms	Applicability of X-ray Analysis	
H-S-H	Hydrogen sulfide	◎	Propane
R-S-H	Mercaptan	◎	
R-S-R	Dialkyl sulfide	○	Gasoline
R-S-S-R	dialkyl disulfide	◎	
	Thiophene	○	Kerosene
	Benzothiophene	○	
	Dibezothiophene	△	Light Oil
	4,6-dibenzothiophene	△	

Petrochemical products and semimanufactured products contain a variety of sulfuric compounds.

For example, Liquefied Petroleum Gas (LPG), a popular fuel for domestic use, contains hydrogen sulfide and mercaptan.

Gasoline or petrol contains a large amount of mercaptan and dialkyl sulfide. However, more recent Gasoline or petrol is employed in the form of reformed gasoline (naphtha), some kinds of which contain thiophenes.

Light Oil contain petrochemical compounds ranging from thiophenes to dibenzothiophenes and, of those dibenzothiophenes, 4,6-dibenzothiophene is generally considered a compound difficult to desulfurize.

Rigaku

Reaction Mechanism in Infinitesimal S Analysis

When the infinitesimal (ppb) S analysis is to be carried out, Rigaku employs a technique of conducting a pretreatment, capturing the S compound and then analyzing it.

This technique is patented under a Rigaku's patent.

To give the full picture of this technique, a sulfuric compound contained in the sample is degraded and activated with strong X-rays. Then, using a catalyst, the activated S compound is reacted with the catalyst, followed by capture of the reacted S compound together with the catalyst.

The analytical measurement of the captured S compound makes it possible to analyze it to a few ppb level.

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Pretreatment for Infinitesimal S Analysis

STEP-1 STEP-2 STEP-3

Catalyst

The infinitesimal S analysis will be described in more detail.

STEP-1:

Catalyst necessary to recover the S compound (manufactured by Rigaku) is added to the sample to be analyzed.

STEP-2:

The sample is irradiated with strong X-rays. This radiation results in degradation and activation of the S compound contained in the sample. At the same time, the S compound in the sample reacts with the nearby catalyst to form a new compound.

STEP-3:

The new sulfuric compound is captured at the bottom of the sample container and is then X-ray analyzed. The sulfuric compound in the sample is in a concentrated sate and, therefore, the analysis of the S compound in the infinitesimal range is possible.

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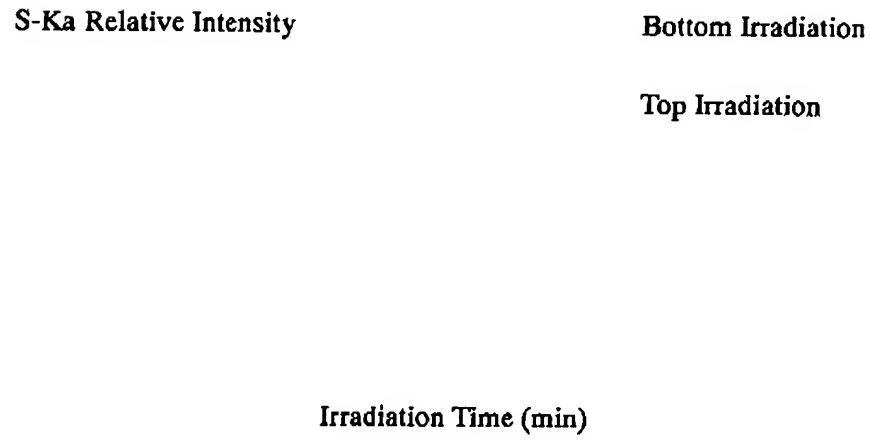
Pretreatment for Infinitesimal S Analysis

Effects of Top and Bottom Irradiation



X-ray irradiation applies when the sulfuric compound contained in the sample is to be reacted with the catalyst. This X-ray irradiation is available in two way; top irradiation and bottom irradiation.

The above illustration shows a chart indicating the effects of those two approaches. The lower the relative intensity, the more notable the reaction and, hence, the more effective.

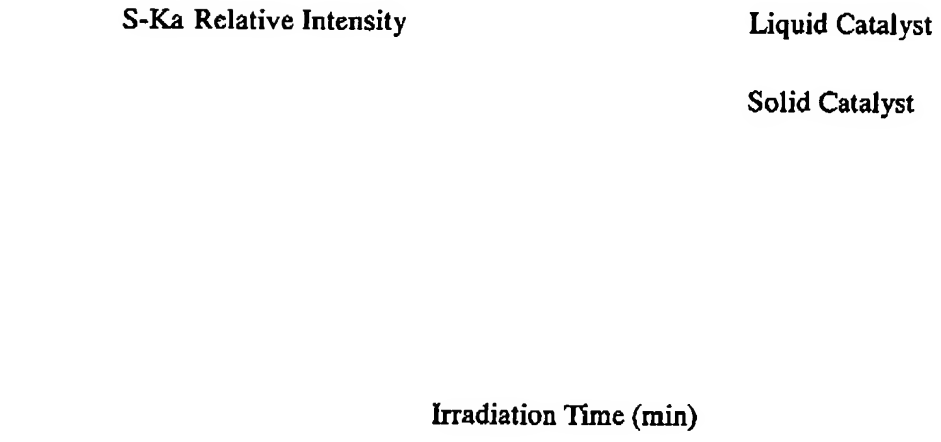
The bottom irradiation allows the effects to show up immediately after the irradiation, but the irradiation over 30 minutes reduces the effectiveness. On the other hand, the top irradiation, even when continued for a large length of time (60 minutes), allows the effectiveness to become notable with passage of time.

Accordingly, the top irradiation appears optimal, but even with the bottom irradiation, the measurement is satisfactory when the irradiation time is limited to 30 minutes or shorter.

Rigaku

Pretreatment for Infinitesimal S Analysis

Effects of Liquid and Solid Catalysts



The above illustration shows a chart indicating effects of the catalysts used to capture the sulfuric compound.

The chart illustrates results of studies conducted on the sulfuric compound left in the sample after the reaction between the sulfuric compound and each of the catalysts. The lower the detection intensity, the more notable the effectiveness.

The chart is based on case examples illustrative of the results of capture with the solid catalyst and the liquid catalyst.

The use of the solid catalyst barely brings about the effects, but the use of the liquid catalyst does the notable effects.

Accordingly, selection of the liquid catalyst appears effective if a high reaction efficiency is expected.

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